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Supporting Information

High Efficient Near-infrared and Semitransparent Polymer Solar Cells Based on an Ultra-Narrow Bandgap Nonfullerene Acceptor

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Materials

Commercially available chemicals were used without further purification. Solvents were dried and distilled from appropriate drying agents prior to use. PTB7-Th was synthesized according to the procedure reported in the literature.[1]

Experimental Section

Measurements: ^{1}H NMR and ^{13}C NMR spectra were measured in $CDCl_3$ on Bruker AV 400 MHz FT-NMR spectrometer. Elemental analysis was carried out on a flash EA1112 analyzer. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA-7. UV-Vis absorption spectra were taken on an Agilent Technologies Cary Series UV-Vis-NIR Spectrophotometer. The electrochemical cyclic voltammetry (CV) was performed on a Zahner Ennium IM6 Electrochemical Workstation with glassy carbon disk, Pt wire, and Ag/Ag$^+$

electrode as working electrode, counter electrode, and reference electrode respectively, in a 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution. DFT calculations were performed by using Gaussian at the B3LYP/6-31G* level. Photoluminescence (PL) spectra was performed on an Edinburgh Instrument FLS 980. The GIWAXS measurements were performed at beamline 7.3.3 at the Advanced Light Source (ALS). Samples were prepared on a Si substrate under the same conditions as those used for device fabrication. The 10 KeV X-ray beam was incident at a grazing angle of 0.12°-0.16°, which maximized the scattering intensity from the samples. The scattered x-rays were detected using a Dectris Pilatus 2M photon counting detector. RSoXS transmission measurements were performed at beamline 11.0.1.2 at the Advanced Light Source (ALS). Samples for R-SoXS measurements were prepared on a PSS modified Si substrate under the same conditions as those used for device fabrication, and then transferred by floating in water to a 1.5 mm × 1.5 mm, 100 nm thick Si_3N_4 membrane supported by a 5 mm × 5 mm, 200 μm thick Si frame (Norcada Inc.). 2-D scattering patterns were collected on an in-vacuum CCD camera (Princeton Instrument PI-MTE). The sample detector distance was calibrated from diffraction peaks of a triblock copolymer poly(isoprene-bstyrene-b-2-vinyl pyridine), which has a known spacing of 391 Å. The beam size at the sample is approximately 100 μm by 200 μm.

The current density-voltage (*J*-*V*) characteristics of the PSCs were recorded with a keithley 2450. The power conversion efficiencies of the PSCs were measured under 1 sun, AM 1.5G (air mass 1.5 global) (100 mw cm^{-2}) using a SS-F5-3A (Enli Technology CO., Ltd.) solar simulator (AAA grade, 50 mm x 50 mm photo-beam size). 2×2 cm^{-2} Monocrystalline silicon reference cell (SRC-00019) was purchased from Enli Technology CO., Ltd. The EQE was measured by Solar Cell Spectral Response Measurement System QE-R3011 (Enli Technology CO., Ltd.). The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell. Atomic force microscopy (AFM) measurements were performed on a Dimension 3100 (Veeco) Atomic Force Microscope in the tapping mode. Transmission electron microscopy (TEM) was performed using a TePNai G2 F20 S-TWIN instrument at 200 kV accelerating voltage, in which the blend films were prepared using a processing technique, as following: first, the blend films were spin-cast on the ITO/PEDOT:PSS substrates; second, the resulting ITO/PEDOT:PSS/ blend films substrates were submerged in deionized water to make these blend films float onto the air-water interface; finally, the floated blend films were taken up on unsupported 200 mesh copper grids for a TEM measurement.

Device fabrication: the PSCs devices were fabricated with an inverted structure of ITO/ZnO/PFN/ PTB7-Th:**ACS8** /MoO_3/Al, which were fabricated and characterized in a N_2-filled glovebox. The ITO-coated glass substrate was cleaned with deionized water, acetone, and isopropanol, respectively. Subsequently, the pre-cleaned ITO-coated glass substrate was treated by UV-ozone for 10 min. Then, the ZnO precursor was spin-coated onto the pre-cleaned ITO glass at 5000 rpm for 40 s and annealed in the titanium plate under 200 ^{o}C for 1 h. Then the PFN at a concentration of 0.2 mg ml^{-1} methanol solution as cathode interlayer was deposited on the ZnO at 2500 rpm for 30 s. The active layer was deposited atop the ZnO layer by spin-coating a toluene solution of PTB7-Th:**ACS8** with a total concentration of 20 mg/mL inside a nitrogen box containing less than 5 ppm oxygen and moisture. Finally, 10 nm MoO_3 and 100 nm Al were sequentially evaporated through a shadow mask to determine the active area of the devices (~0.0665 cm^2) in the vacuum chamber under a pressure of ca. 4×10^{-4} Pa.

The structure of semitransparent PSC was ITO/ZnO/PFN/PTB7-Th:**ACS8**(1:2, w/w)/MoO_3/Au/Ag. Patterned ITO glass (sheet resistance = 15 $\Omega\ \square^{-1}$) was precleaned in an ultrasonic bath with acetone and isopropanol, and treated in an ultraviolet-ozone chamber for

10 min. ZnO layer (ca. 30 nm) was spin-coated at 5000 rpm for 40s onto the ITO glass from ZnO precursor solution, and then baked at 200 °C for 60 min. Then the PFN at a concentration of 0.2 mg ml^{-1} methanol solution as cathode interlayer was deposited on the ZnO at 2500 rpm for 30 s. A PTB7-Th:**ACS8** mixture (20 mg mL^{-1} in total) in toluene was spin-coated at 1300 rpm on the ZnO layer to form a photoactive layer (ca. 100 nm). The MoO_3 layer (ca. 8 nm), Au seed layer (ca. 1 nm), and ultrathin Ag electrode (ca. 10, 15, 20 nm) were slowly evaporated onto the surface of the photoactive layer under vacuum (ca. 10^{-5} Pa). In the case of the 1 nm Au layer, the layer is probably not homogeneous, so the thickness given here means nominal or equivalent thickness, indicating the amount of material on the sample. The light intensity at each wavelength was calibrated using a standard single crystal Si photovoltaic cell.

The average visible transmittance (AVT) was calculated from visible transmission spectra measured by Agilent Technologies Cary Series UV-Vis-NIR Spectrophotometer. AVT is estimated as the simple arithmetic mean value of the transmittance in 370-740 nm region (The data pitch is 2 nm).

$$\mathrm{AVT}=\frac{\int T(\lambda)P(\lambda)S(\lambda)d(\lambda)}{\int P(\lambda)S(\lambda)d(\lambda)}$$

Where λ is the wavelength, T is the transmission, P is the photopic response, and S is the solar photon flux (AM1.5G) for window applications, or 1 for other applications.[2]

Mobility measurements: The hole and electron mobility were calculated by using the space-charge-limited current (SCLC) method.

$$J = 9\varepsilon_0\varepsilon_r\mu(V_{\mathrm{appl}} - V_{\mathrm{bi}} - V_{\mathrm{s}})^2/8L^3$$

Where J is the current density, ε_0 is the permittivity of free space (8.85×10^{-12} F m^{-1}), ε_r is the relative permittivity of the material (assumed to be 3), μ is the mobility of hole or electron,

V_{appl} is the applied voltage, V_{bi} is the built-in voltage (0 V), V_s is the voltage drop from the substrate's series resistance (V_s = IR) and L is the thickness of the active layer.

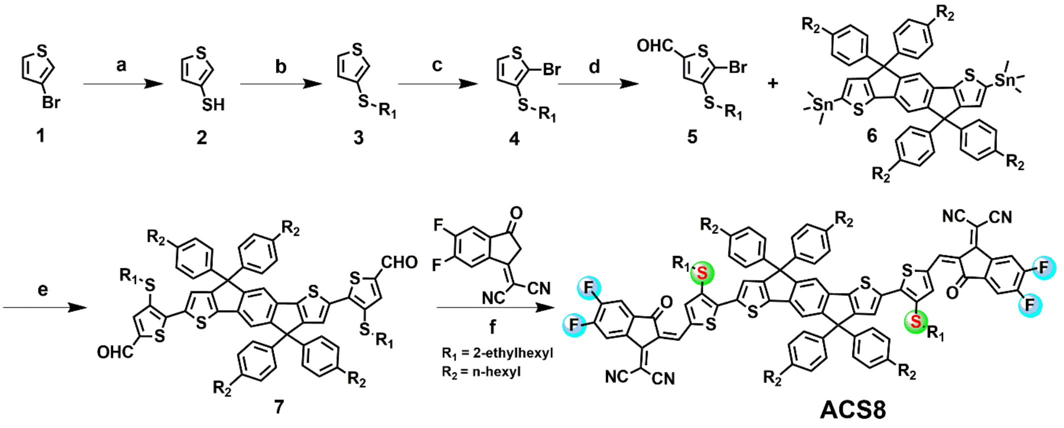
Synthesis

Compound 1 were purchased from commercial sources. Compound 2, compound 3 and compound 4 were synthesized according to reported method.[3] Compound 5, compound 6 compound 7 and **ACS8** were synthesized as follows:

Synthesis of **5-bromo-4-((2-ethylhexyl)thio)thiophene-2-carbaldehyde (compound 5)**: LDA was added dropwise in the solution of compound 4 (2 g, 6.5 mmol) in anhydrous THF (100 mL) at -78 °C under argon atmosphere. The mixture was stirred for 2 h at low temperature, and then DMF (2 mL) was added, 15 min later, the low temperature bath was removed and allow the reaction was stirred in the room temperature for 10 h. Then the mixture was quenched by water and extracted by dichloromethane three times. After the combined organic phase was concentrated, further purification was carried out by silica gel column chromatography by using petroleum/dichloromethane (5:1) as eluent to give pure compound 5 was obtained as green oil(1 g, 50%). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 9.76 (s, 1H), 7.57 (s, 1H), 2.89-2.88 (d, 2H), 1.57-1.23 (m, 9H), 0.91-0.86 (m, 6H): ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 181.35, 142.85, 137.96, 136.45, 125.41, 39.59, 39.25, 32.10, 28.70, 25.36, 22.88, 14.04, 10.71. GC-MS m/z: [M+H+] calcd. for $C_{13}H_{20}BrOS_2$, 335.01 (100%), 337.01 (97%); found 336.06.

Synthesis of **5,5'-(4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b']-dithiophene-2,7-diyl)bis(4-((2-ethylhexyl)thio)thiophene-2-carbaldehyde) (compound 7)**: Compound 7 was synthesize by conventional stile coupling reaction. Compound 5 (302 mg, 0.9 mmol), compound 6 (375 mg, 0.3 mmol) and catalyst ($Pd(PPh_3)_4$) (35mg, 0.03mmol) was added into a 50 mL two necked flask, and 20 mL of toluene was added. The mixture was purged with argon for 5 min. And then the reaction was moved to 110 °C oil bath and stirred for 24 hours. Then the mixture was quenched by water and extracted by chloroform three times. and the crude product was purified by silica gel column chromatography by using petroleum/dichloromethane (3:1), orange-red solid (210 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 9.79 (s, 2H), 7.65(s, 2H), 7.50-7.48 (d, 4H), 7.18-7.16 (d, 8H), 7.09-7.07 (d, 8H), 2.87-2.85 (d, 4H), 2.58-2.54 (t, 8H), 1.60-1.22 (m, 50H), 0.87-0.83 (m, 24H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 181.87, 156.06, 153.83, 146.16, 144.83, 141.75, 141.28, 138.71, 137.02, 135.45, 129.18, 128.42, 127.78, 124.00, 117.86, 62.98, 41.05, 39.38, 35.54, 32.15, 31.68, 31.31, 29.11, 28.69, 25.50, 22.90, 22.56, 14.04, 10.71. MALDI-TOF-MS m/z: [M] calcd. for $C_{90}H_{110}O_2S_6$, 1415.69; found, 1415.92. The **compound 7** was collected by filtration and dried under vacuum. Anal. Calcd (%) for $C_{90}H_{110}O_2S_6$: C, 76.33; H, 7.83; found: C, 76.15; H, 7.85.

Synthesis of **compound ACS8**: To a mixture of compound 5 (240 mg, 0.169 mmol) and 3-(1,1-dicyanomethylene)-5,6-difluoro-1-indanone (312 mg, 1.36 mmol) (compound 6) in 30 mL chloroform, pyridine (1 mL) was added at room temperature. Then the mixture was placed in an oil bath at 75 °C and stirred for another 16 h. The mixture was precipitated into methanol and filtered through a Buchner funnel, and the solid was washed by methanol. Then the product of **ACS8** (150 mg, yield 89%) was purified by silica gel column chromatography by using petroleum/dichloromethane (2:1) as eluent. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.71 (s, 2H), 8.56-8.52 (m, 2H), 7.73-7.65 (m, 6H), 7.53 (s, 2H), 7.21-7.19 (d, 8H), 7.12-7.10 (d, 8H), 2.95-2.94 (d, 4H), 2.60-2.56 (t, 8H), 1.62-1.26 (m, 50H), 0.87-0.83 (m, 24H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 186.13, 157.98, 157.36, 154.75, 152.34, 149.70, 147.58, 145.88, 141.98, 140.89, 137.75, 136.60, 135.91, 133.39, 131.61, 128.58, 127.87, 125.14, 121.55, 118.26, 115.08, 114.93, 114.18, 114.09, 112.68, 112.65, 70.01, 62.99, 41.02, 39.42, 35.59, 32.13, 31.60, 31.20, 25.49, 22.95, 22.53, 14.11, 10.88. MALDI-TOF-MS m/z: [M] calcd. for $C_{114}H_{114}F_4N_4O_2S_6$, 1839.72; found, 1839.87. The **ACS8** was collected by filtration and dried under vacuum. Anal. Calcd (%) for $C_{114}H_{114}F_4N_4O_2S_6$: C, 74.39; H, 6.24; N, 3.04; found: C, 74.11; H, 6.25; N, 3.03.



Scheme S1. Synthetic routes of ACS8: (a) n-BuLi, THF, -78 °C; sulfur, -78 °C. (b) $(CH_3)_3COK$, EtOH, 0 °C; 3-(bromomethyl) heptane, 90 °C. (c) DMF, NBS, 0 °C. (d) LDA, THF, -78 °C; DMF, -78 °C. (e) Pd $(PPh_3)_4$, toluene, 110 °C. (f) pyridine, $CHCl_3$, 75 °C.

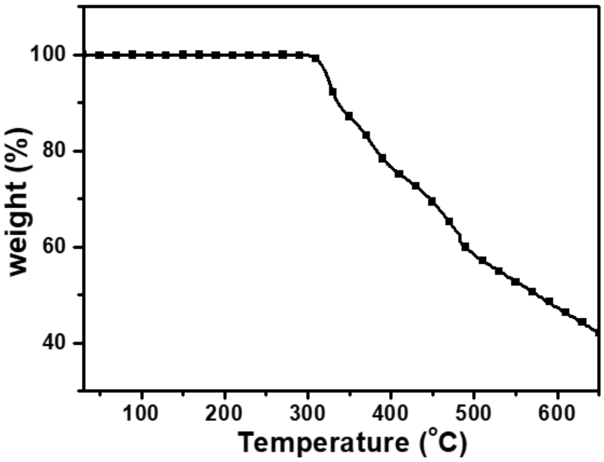


Fig. S1. TGA plot curve of ACS8 with a heating rate of 10 ºC min^{-1} under nitrogen atmosphere.

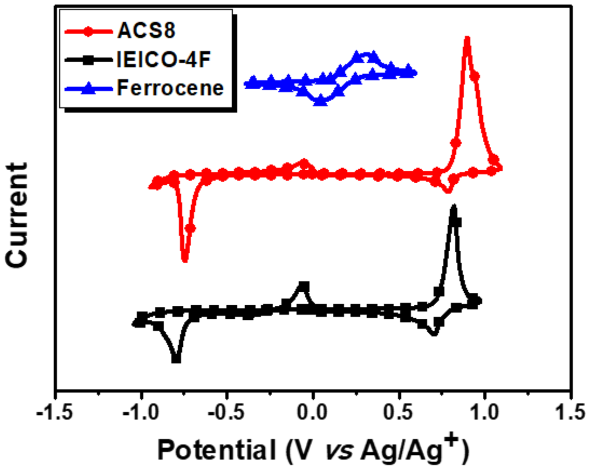


Fig. S2 Cyclic voltammograms of ACS8 and IEICO-4F.

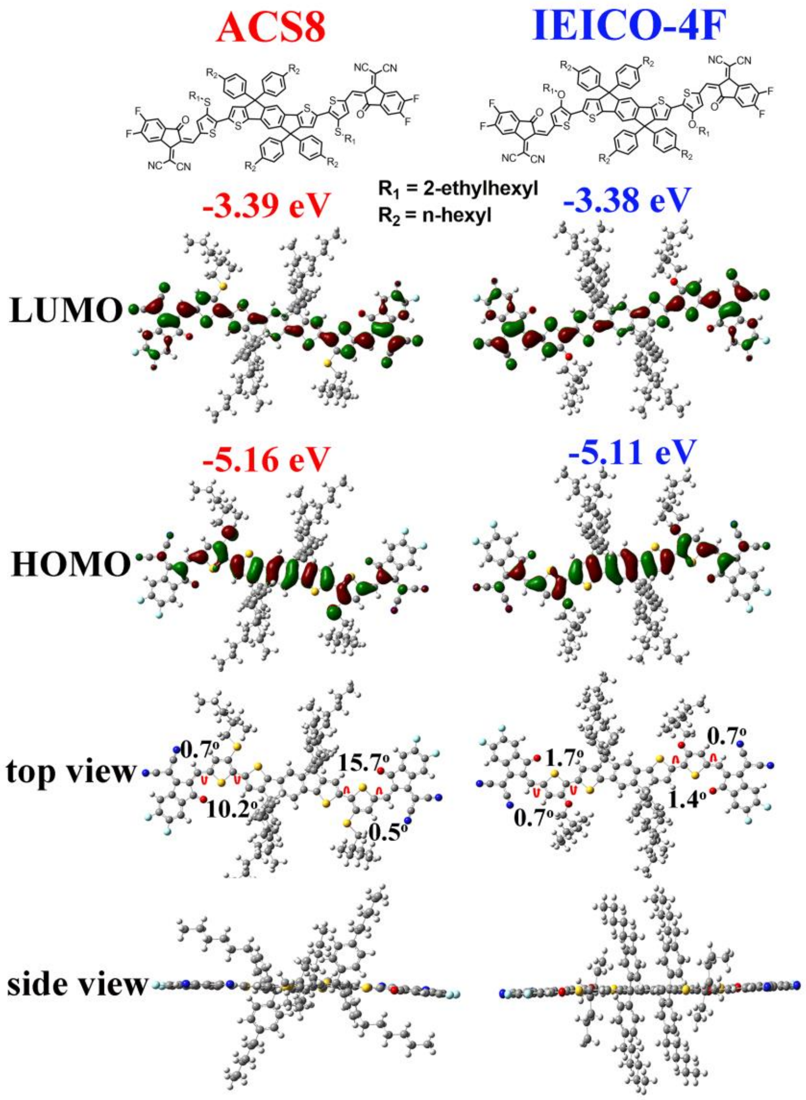


Fig. S3. The chemical structures, LUMO and HOMO distributions and optimal geometries and of ACS8 and IEICO-4F calculated at B3LYP/6-31G* level.

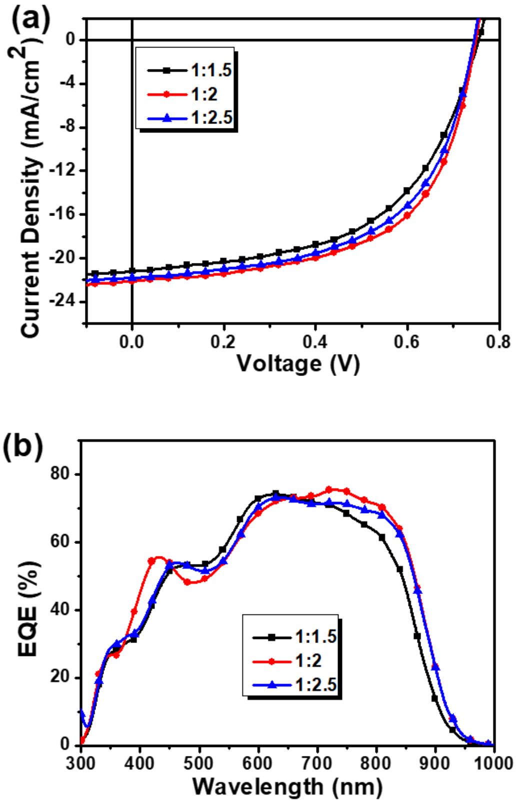


Fig. S4. (a) The *J-V* characteristics and (b) the corresponding EQE curves of the PSCs based on PTB7-Th:ACS8 with different D/A weight ratios (w/w).

Table S1. Photovoltaic parameters of the PSCs based on PTB7-Th:ACS8 with different D/A weight ratios (w/w) under the illumination of AM 1.5G, 100 mw/cm^2.

D/A ratio	V_{oc} (V)	$J_{sc}{}^a$ (mA cm^{-2})	FF (%)	PCE^b (%)
1:1.5	0.76	21.2(19.9)	54.2	8.7(8.5±0.2)
1:2	0.75	22.1(21.0)	58.8	9.8(9.6±0.2)
1:2.5	0.75	21.8(20.7)	57.2	9.3(9.2±0.1)

[a] Values calculated from EQE in brackets. [b] Average PCEs in brackets for over 30 devices.

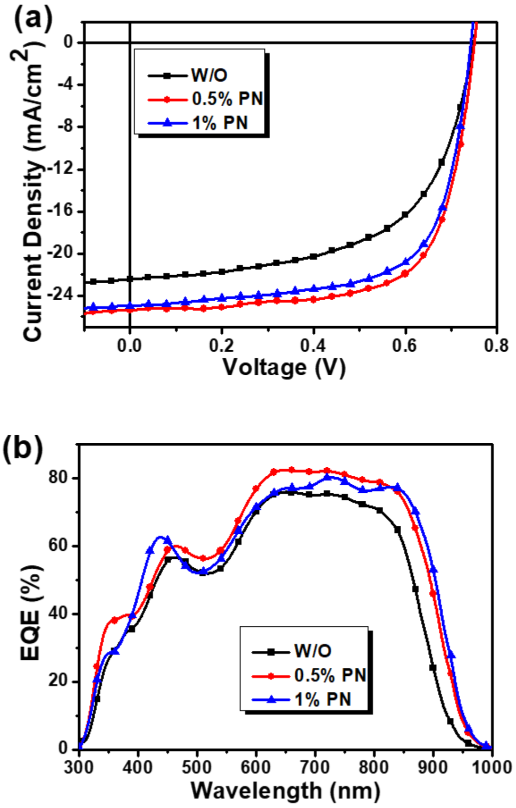


Fig. S5. The *J*-*V* characteristics of the PSCs based on PTB7-Th:ACS8 (1:2, w/w) with different contents of PN under the illumination of AM 1.5G, 100 mw cm^{-2}.

Table S2. Photovoltaic parameters of the PSCs based on PTB7-Th:ACS8 (1:2, w/w) with different contents of PN under the illumination of AM 1.5G, 100 mw cm^{-2}.

Contents (V/V, %)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
0	0.75	22.5(21.3)	58.8	9.9(9.7±0.2)
0.5	0.75	25.3(24.2)	69.3	13.2(13.1±0.1)
1	0.74	25.0(23.7)	67.4	12.5(12.3±0.2)

[a] Values calculated from EQE in brackets. [b] Average PCEs in brackets for over 30 devices.

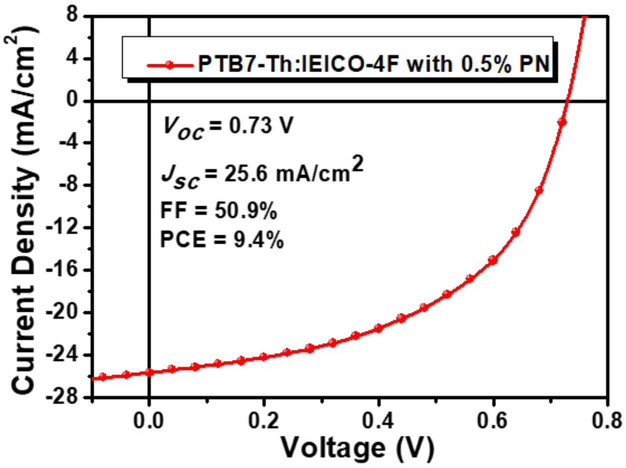


Fig. S6. The *J-V* characteristic of the PSC based on PTB7-Th:IEICO-4F (1:2, w/w) with 0.5% PN under the illumination of AM 1.5G, 100 mw cm^{-2}.

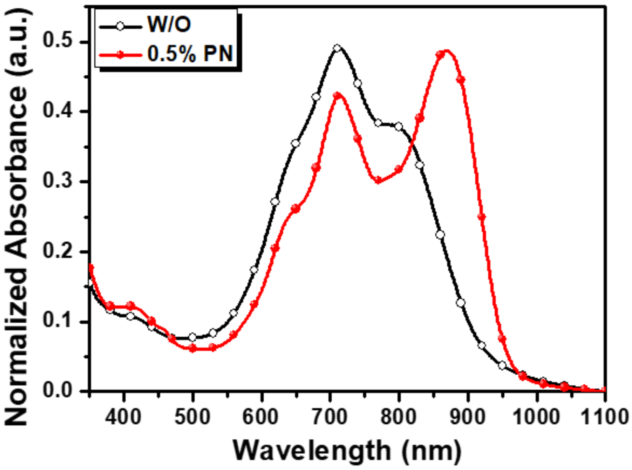
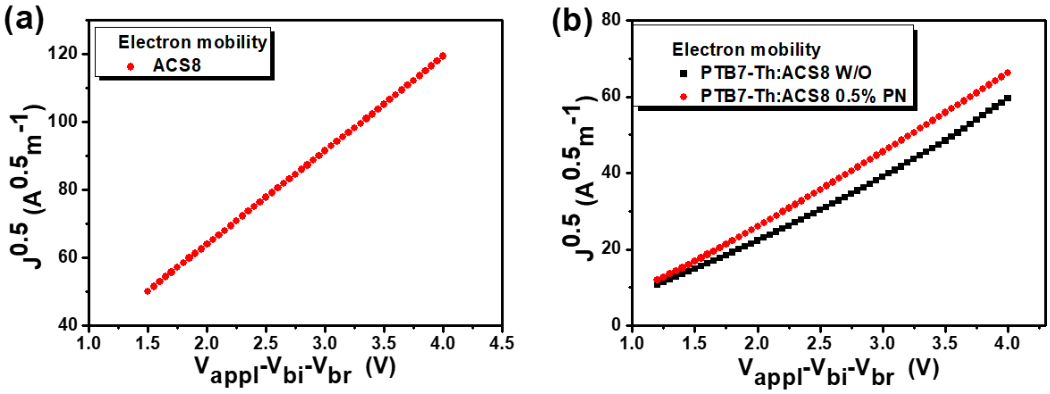


Fig. S7. The UV-Vis absorption spectra of the blend films based on PTB7-Th: ACS8 (1:2, w/w) blend film without PN or with 0.5% PN.



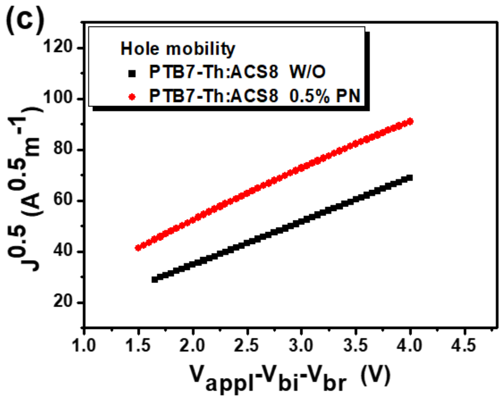


Fig. S8. Curves obtained from the (a) electron-only based on pure ACS8, (b) electron -only, and (c) hole-only devices based on the PTB7-Th:ACS8 (1:2, w/w) without PN or with 0.5% PN according to the SCLC model.

Table S3. Charge mobilities of the device active layers measured by SCLC method.

Treatments	μ_h (cm^2 V^{-1} s^{-1})	μ_e (cm^2 V^{-1} s^{-1})	μ_h /μ_e
ACS8[b]		2.65 × 10^{-4}	
PTB7-Th:ACS8[a]	1.47 × 10^{-4}	1.30 × 10^{-4}	1.13
PTB7-Th:ACS8[b]	2.25 × 10^{-4}	2.01 × 10^{-4}	1.12

[a] w/o , [b] 0.5% PN.

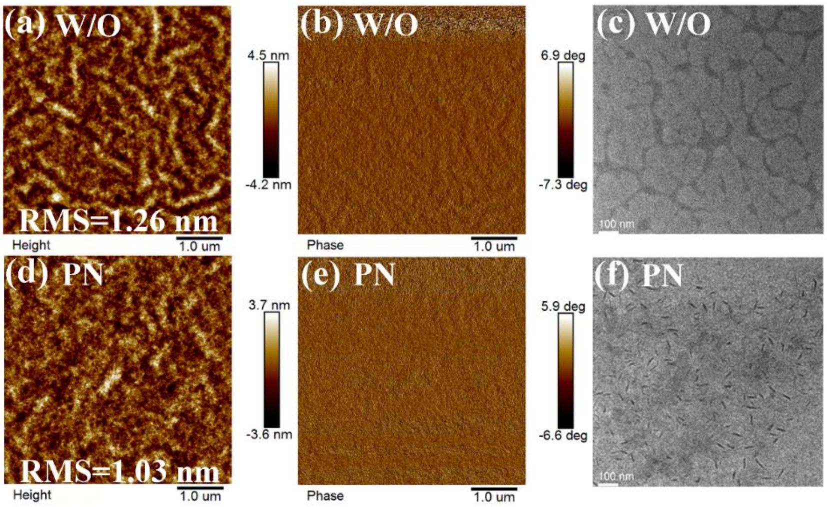


Fig. S9. The AFM and TEM images of the PTB7-Th:ACS8 blend films: (a), (b) and (c) for the blend without PN treatment; and (d), (e) and (f) for the blend with 0.5%PN treatment.

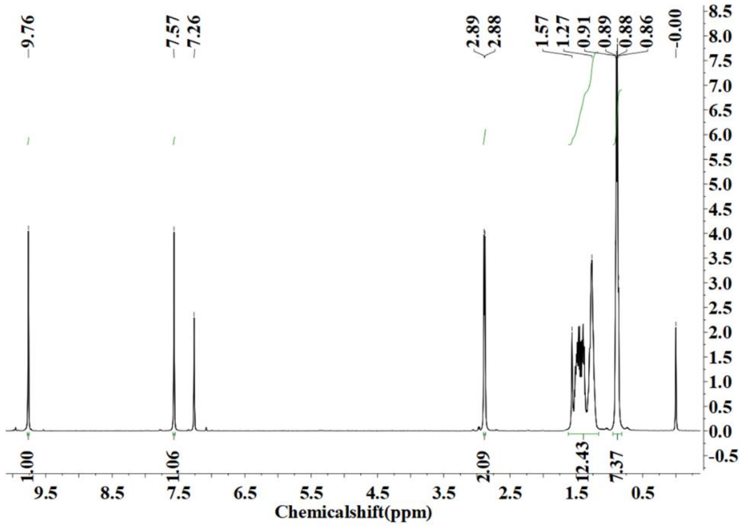


Fig. S10. ^{1}H NMR spectrum of compound 5 in $CDCl_3$.

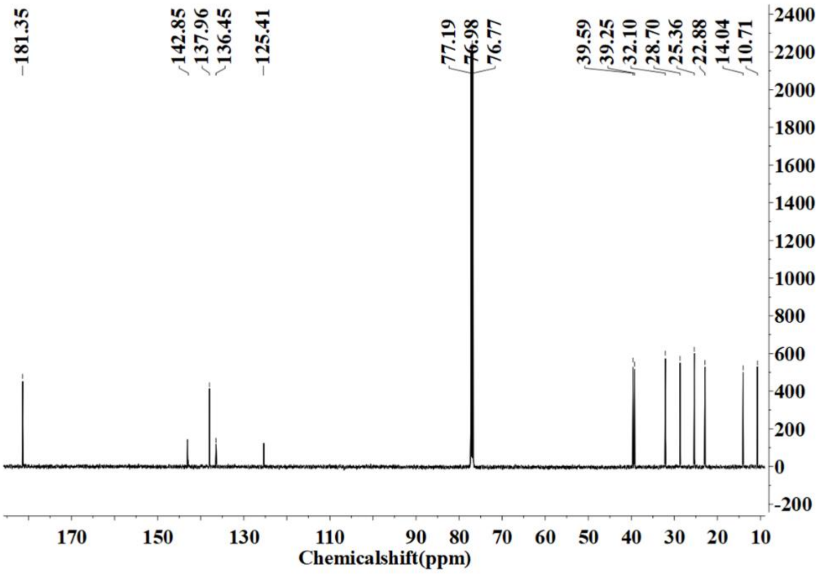


Fig. S11. ^{13}C NMR spectrum of compound 5 in $CDCl_3$.

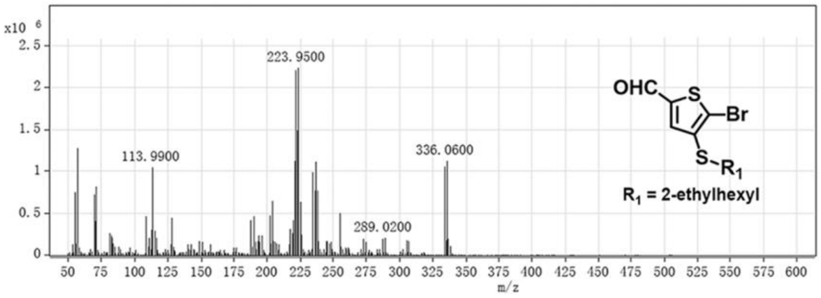


Fig. S12. GC-MS polt of compound 5.

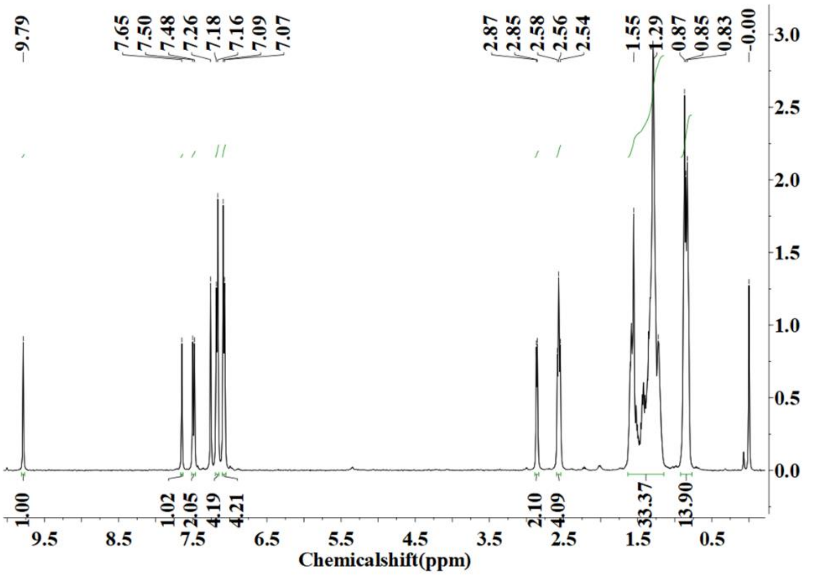


Fig. S13. ^{1}H NMR spectrum of compound 7 in $CDCl_3$.

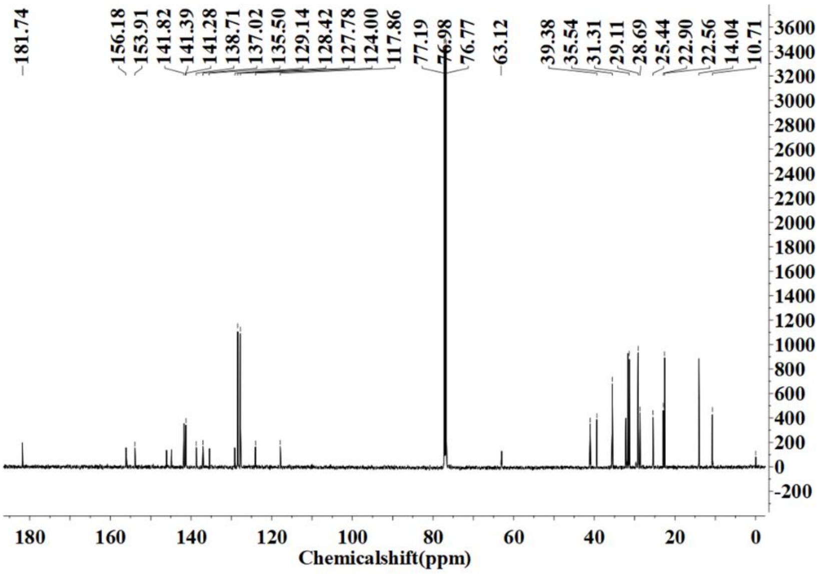


Fig. S14. ^{13}C NMR spectrum of compound 7 in $CDCl_3$.

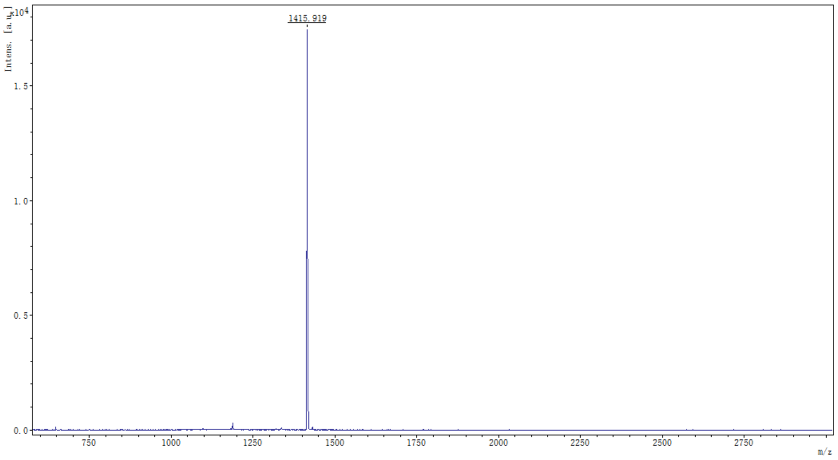


Fig. S15. MALDI-TOF plot of compound 7.

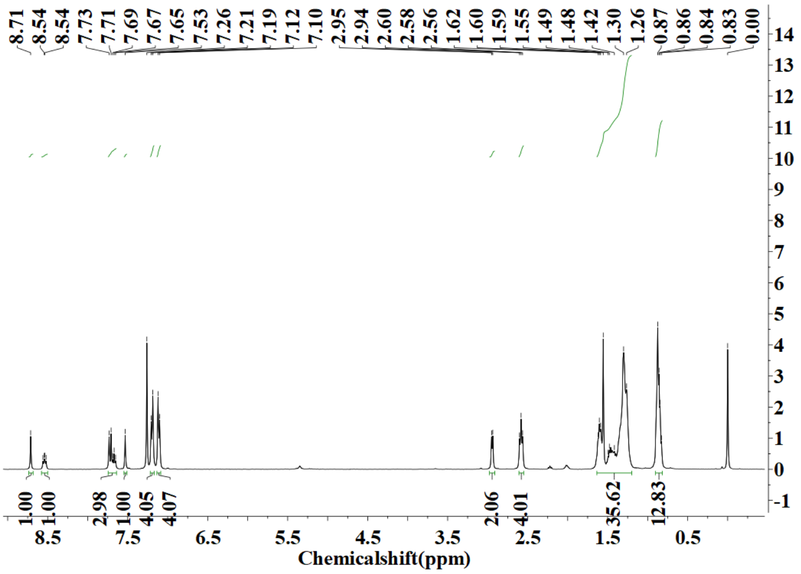


Fig. S16. ^{1}H NMR spectrum of compound ACS8 in $CDCl_3$.

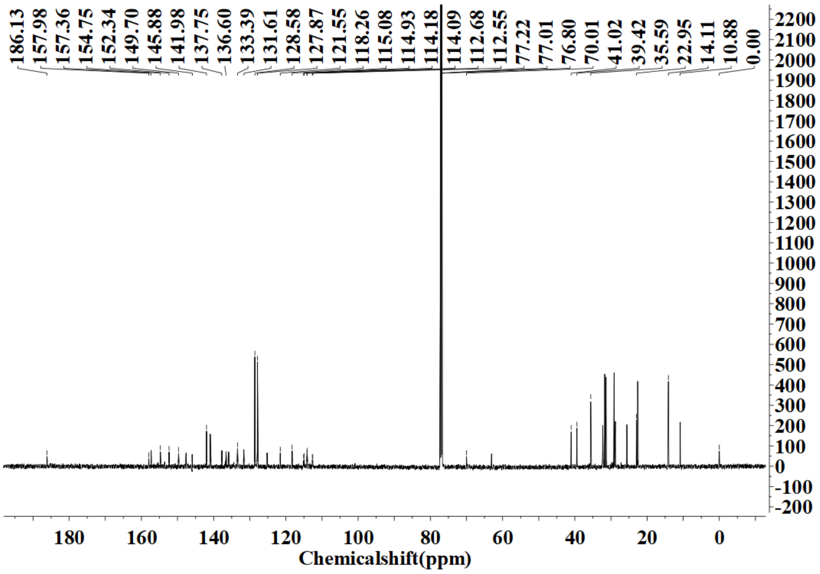


Fig. S17. ^{13}C NMR spectrum of compound ACS8 in $CDCl_3$.

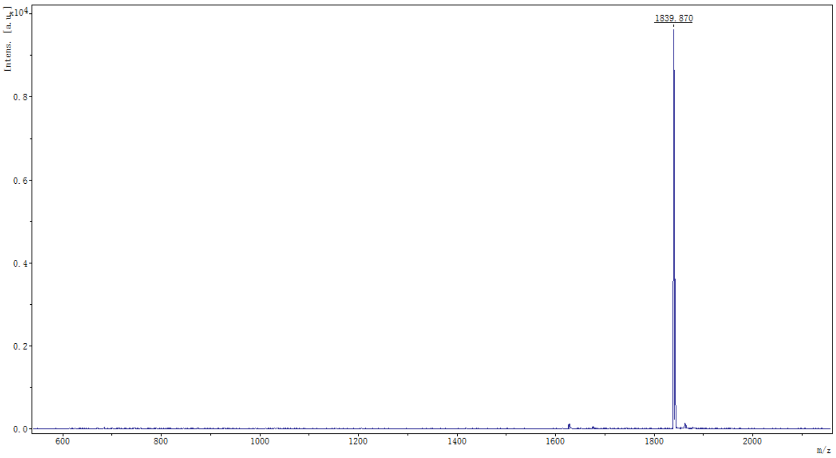


Fig. S18. MALDI-TOF plot of compound ACS8.

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